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(54) SOLIDIFICATION OF MOLTEN SULPHUR

(71) I, HERBERT JAMES ELLIOTT, of 63 Poulton Estate, Bradford-on-Avon, Wiltshire, a British subject, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with the solidification of molten sulphur, and in particular the pelletizing of sulphur. Natural sulphur is usually extracted by techniques which result in large quantities of molten sulphur. It is desirable for packaging and transportation that the sulphur should be in an easily manageable solid form. Pellets are a particularly attractive solid form if the generation of hazardous fires can be avoided both during pelletization and subsequent handling. It is also desirable for sulphur obtained in other solid forms, for example powders or slurries resulting from desulphurization processes and bulk solid sulphur in sulphur "vats", to be converted to pellets for further handling. It is particularly important that the sulphur pellets should have sufficient mechanical strength to withstand transportation and mechanical handling.

Various processes have been proposed for pelletizing sulphur, in which droplets of molten sulphur are formed in a coolant such as water, and the droplets solidified into pellets.

U.S. Patent No. 3,334,159 (Campbell) describes a process in which molten sulphur is allowed to pass through a prilling head in the form of a perforated metal plate into a coolant tank. It has been found that this form of prilling head generates pellets of undesirably small size which are easily windborne.

U.S. Patent No. 3,504,061 (Elliott) describes a process in which molten sulphur is poured into a tank in which the water coolant is swirled to prevent solidifying pellets from agglomerating. The pellets obtained are of a more satisfactory size but contain a characteristic J-shaped perforation which both weakens the pellet and provides a moisture trap.

The present invention provides a sulphur pelletizing process in which pellets are produced by solidifying molten sulphur droplets in a coolant and the pellet is consolidated and internal cavities modified by allowing the solidifying pellet/droplet to contact a ramp submerged in the coolant while still in an at least partially molten condition or to be subjected to acoustic pressure waves.

These two treatments may advantageously be combined by mounting an acoustic pressure wave generator on the ramp at a submerged or above-surface portion thereof. Alternatively, with or without the presence of a ramp, the generator may be mounted anywhere in the coolant tank so that the pressure waves are transmitted to the solidifying droplets through the coolant.

The molten material may be fed to the coolant as a continuous stream or as molten droplets. In the former case, the stream will normally break up into molten droplets below the surface of the coolant.

The term "acoustic pressure waves" is intended to include pressure waves of both sonic, and, more preferably, ultra sonic frequency. The former may be generated by a mechanical vibrator, the latter by an ultra sonic transducer.

The cavity modification achieved by the present invention is to change the J-shaped cavity to a more centrally positioned substantially circular cavity which has less of a weakening effect on the pellet. The modification is believed to result from substantially radially inward consolidating forces exerted on the solidifying pellet by contact with the ramp and/or the action of the acoustic pressure waves.

The invention will now be described in more detail with reference to the accompanying drawings, in which:—

FIGURE 1 is a diagrammatic side elevation of a basic apparatus for demonstrating the parameters of the present invention;

FIGURE 2 shows a nozzle for feeding molten sulphur;

FIGURE 3 shows a gully feed means for molten sulphur;

FIGURE 4 is a sectional side elevation of

a pelletizing installation embodying the present invention; and

FIGURE 5 is a sectional side elevation of a further pelletizing installation embodying the present invention.

Figure 1 of the accompanying drawings illustrates the basic parameters of the preferred embodiment of the present invention. A tank 1 contains water 2 as coolant. A ramp 3 is submerged in the water, optionally with an upper portion *3a* extending above the water surface. An ultra sonic transducer 4 is attached to the underside of the ramp 3. Alternatively, a transducer *4a* may be mounted in portion *3a* of the ramp 3 to allow easier access for maintenance, although the low power consumption of typical units make for minimal maintenance. As a further alternative a transducer *4b* may be mounted at the base of the tank and this allows the operating option of pelletizing without the ramp but under the influence of the transducer. Molten sulphur 5 is delivered from a reservoir 6 via a nozzle or gully (or a droplet forming head if so desired). A continuous stream of molten sulphur breaks up into droplets below the water surface and the feed is positioned so that the droplets come under the influence of the ramp before they have solidified. As the droplets move down the ramp their vertical velocity is reduced so they reach a degree of solidification at which they will not agglomerate on contact in a shorter depth of water than would be needed if the ramp was absent and solidification took place under free fall conditions. Solidified pellets fall from the ramp into a sump 7, from which they may be discharged by any conventional means and dewatered.

As mentioned earlier, the effect of the ramp is to consolidate the pellet and reduce the cavity which is inherent in pellets produced by solidifying molten droplets in a liquid coolant. Since the ramp also slows the falling velocity of the pellets, the feed rate of molten material onto the ramp must be kept at a level which will avoid undue agglomeration of the pellets before complete solidification. In practice it has been found that a suitable feed rate for an unbroken stream of molten sulphur poured into water is in the range of about 0.4 to about 0.6 long tons per day. A small degree of agglomeration is not necessarily undesirable as agglomerations produced from a small number of pellets tend to form a sausaged shaped pellet which is in some ways advantageous, for example in terms of the angle of repose adopted by a stockpile. Accordingly increasing the rate of feed of molten sulphur does allow to some extent variation of the pellet size.

When a ramp is used in conjunction with an ultrasonics transducer unit it will normally be of metal, preferably stainless steel, of about 1/16 inch thickness. The ultrasonic pressure waves prevent adhesion of the pellets to the ramp. When a ramp is used alone then the material must be chosen so that pellets do not adhere. In this respect glass, preferably wire-reinforced, has been found to be a particularly suitable material. Other suitable materials may easily be selected by routine experiment.

The preferred angle of the ramp for normal working lies in the range of about 45 to 65° to the horizontal. If the coolant depth or pellet fall velocity is desired to be reduced further the angle of the ramp can be reduced to about 25°, but the feed rate of molten sulphur will need to be reduced accordingly as mentioned above.

The length of the ramp must be such that pellets leaving the ramp are sufficiently solidified so that they will not adhere to each other in the sump. The actual length selected will depend on the particular operating conditions such as sulphur feed temperature and water coolant temperature, pellet fall velocity (ramp angle) etc. Normally pellets will require to traverse about 9 to 18 inches of ramp to reach the desired solidification and ramps of 12 to 36 inches length may be used.

The ultrasonic transducers used to condition the solidifying pellets, alone or in combination with a ramp as described above, are preferably transducer units rated at from 10 to 50 watts at a frequency of about 25 Khz. The transducers may be positioned in the base of the coolant tank, or, when a ramp is used, on the ramp above or below the coolant surface or at a location in the coolant spaced from the ramp. The positioning is not of critical importance provided that the ultrasonic pressure waves are brought to bear on the solidifying pellets. Depending on the power of the transducers used, one transducer may be used for each molten droplet/pellet stream or they may be spaced at wider centres.

Pouring an unbroken molten sulphur stream into water usually results in pellets in which the major proportion are in the size range of 1/16 to 3/32 inches diameter. It has been found that when the molten stream falls directly over an ultrasonic transducer then the molten droplets are broken into much finer pellets before solidifying. In some applications this can be advantageous, for example in the production of insoluble sulphur where extensive grinding and milling is necessary to produce powdered sulphur. However, for normal purposes fines of this nature are to be avoided and so the molten sulphur stream preferably enters the coolant away from the major region of influence of the transducer, and enters this region only after partial solidification of the pellet has taken place.

The temperature of the water coolant may range from just above freezing point to about 140°F (60°C) but is preferably maintained at 70 to 100°F (21 to 38°C). The preferred

molten sulphur feed temperature is about 130 to 140°C. 125 to 130°C may also be used but preferably not by delivering through nozzles to avoid solidification and blockages at the nozzle exit. If these lower temperatures are used, delivery is preferably by a bifurcated gully as described in more detail below. In the production of insoluble sulphur then feed temperatures of above 160°C are necessary to ensure the transition of sulphur to the insoluble form. Because of the anomalously high viscosity of sulphur at around 160°C, temperatures in considerable excess of this are normally used in the production of insoluble sulphur, so that the molten sulphur delivery must take place under a blanket of an inert gas.

The depth of the coolant will depend on the length and angle of the ramp when used. If no ramp is used, then the depth must be such as sufficiently to solidify the pellets to prevent mutual adhesion when they collect in a sump at the base of the coolant tank.

The depth of water cover above the ramp is preferably about 4 to 6 inches at the point of delivery of the molten sulphur, but this depth may be varied to alter the shape of product obtained. For example, reducing the water cover allows the molten droplets to contact the ramp in a substantially molten form, rather than the preferred partially solidified form, and this can deform the droplet to produce tablet or pastille shaped pellets, rather than the normal substantially spherical pellets. In some circumstances, for example in angle of repose of a stockpile, the tablet shaped pellets can be advantageous.

It is possible to accommodate higher sulphur feed temperatures and higher coolant temperatures, or alternatively to obtain earlier solidification and hence use less coolant depth and/or a shorter ramp at lower temperatures, by incorporating a silicone fluid, e.g. a dimethyl polysiloxane or, more preferably, a methyl phenyl polysiloxane, into the molten sulphur. This technique forms the subject of copending Application Serial No. 10473/76 (Serial No. 1,536,694), the disclosure of which is incorporated herein by reference.

The molten sulphur may be delivered to the coolant in any suitable manner which results in formation of molten droplets within the coolant. For example, molten sulphur may be dispensed from a reservoir in droplet form from a conventional droplet-forming head. However, it is preferred to introduce molten sulphur into the coolant as an unbroken stream in view of the greater feed rate and mechanical simplicity achievable by this technique. The molten sulphur stream breaks up into droplets shortly below the coolant surface as already described in the above noted prior U.S. Patents, and the feed means of both those Patents may be used in the present invention.

However, it has been found that preferred results are obtained using a nozzle as shown in Figure 2 of the accompanying drawings. The nozzle comprises a body 11 having a main bore 12 and exit bore 13. A screw thread 14 and flanged head 15 with cross-cut 16 allow the nozzle to be screwed into the base of a molten sulphur reservoir. The nozzle may be provided with an upwardly extending shield 17 (shown in broken lines) to prevent solid impurities which may accumulate in the reservoir flow from entering the nozzle bore. The particular feature of this nozzle is the ratio of the length to diameter of the exit bore 13. In previous nozzles of this type the length of the exit bore has been considerably greater than its diameter, at a ratio of e.g. 9:1. In the present instance with a diameter of 1.5 to 2.5 mm an exit bore length of about 1 mm is used so that the diameter to bore length ratio is from 1.5 to 2.5:1. With molten sulphur the indicated dimensions produce a suitably stable unbroken stream which breaks up into a particularly suitable size range of droplets/pellets. Such nozzles are positioned in a molten sulphur reservoir at spacings which avoid contact of the various streams of molten droplets produced in the coolant, typically 1½ to 3 inches.

The feed height from nozzle to coolant surface is typically 4 to 6 inches. This may be increased if desired provided that the stability of the stream can be maintained.

An unbroken stream may also be delivered from a gully as shown at 21 in Fig. 3 of the accompanying drawings.

The gully 21 has a V or U-shaped cross section with two forwardly extending portions extending from the discharge end (typically at 55 to 60°) which form the boundary of the V or U-shaped portion. The base of the gully slopes upward to the discharge end (typically at about 20°).

A gully of this type may be made by cutting a V or U-shaped notch in a sheet of metal and then bending the sheet along a line passing through the apex of the notch to form a V or U-shaped gully.

The flow of molten material can be readily controlled by spreading or bending towards each other the bifurcated "wings" of the spout. In particular it has been found that when the stream of liquid is reduced in speed or cut off completely, the liquid does not normally run back along the external surface of the spout as is common with conventional spouts. Also any obstructions are easily removed from the open gully.

Molten sulphur is supplied to the gully 21 from a trough 22 having a steam jacket 23 which has an outer coating 24 of magnesia lagging. One wall of the trough has a plurality of apertures 25 which allows the exit of molten sulphur which falls via a channel 26 in the steam jacket to a plurality of gullies 21, which

as described earlier have an upwardly directed base and a V-shaped pour exit. Most solid impurities sink to the base of the trough and do not reach the apertures 25. Any that do reach and obstruct the gully may be easily cleared.

In any delivery system, the head of sulphur in the reservoir may be kept at constant level by a simple weir control or by level-detecting devices controlling inlet valves.

Examples of installations incorporating the principles outlined above are shown in Figures 4 and 5 of the accompanying drawings.

In Figure 4 a coolant tank 31, which may be cylindrical or rectangular, is supported on framework 32. Water is fed into the tank 31 from feed pipes 33 and is removed for cooling and return by weir overflows 34. Molten sulphur 36 is held in a trough 35, which may be annular or rectangular, supported over the coolant tank. The trough 35 is surrounded by a steam jacket 37 and the base of the trough contains nozzles 38 as shown in Figure 2. The molten sulphur falls in unbroken streams from the nozzles into the water coolant where it breaks up into molten droplets. The head of molten sulphur in the trough may be maintained constant by known level controls such as weir overflows. The pellets partially solidify as they fall through the coolant and then contact a ramp portion 39, which may be attached to the side of the tank in the inclined sidewall configuration shown. The ramp and coolant are activated by ultrasonic transducers 40 attached to the outside of the tank. The solidification of the pellets is completed as they travel over the ramp, and after solidification they fall into a sump 41, here formed by the conical or inclined base of the tank.

The pellets are carried by a current of water from pipe 42 into and up pipe 43 and discharged onto a conveyor 44 passing over the tank. The conveyor is perforated or of wire mesh to allow drainage of the pellets which are then conveyed for further drying or storage.

In Figure 5 a cylindrical coolant tank 51 has a conical base 52 to form a sump. Molten sulphur is fed as in Figure 4 in continuous streams to the coolant tank 51 from a steam-jacketed head 53 fitted with nozzles 54 as shown in Figure 3. Fresh coolant is fed to the tank 51 from reservoir 55 via inlet 56 and warmed coolant is removed from weir overflows 57. The molten droplets formed just below the coolant surface are allowed to solidify as they fall through the coolant and then accumulate in the sump 52. The falling solidifying pellets may be subjected to pressure waves from ultrasonic transducers attached to the tank walls or immersed in the coolant, although as mentioned above satisfactory pellets can be obtained with this feed system if the pellets are allowed to fall freely.

When a sufficient quantity of pellets have accumulated, they are discharged, together with some coolant, by gravity through valve 58 into holding tank 59. In the holding tank 59 the pellets are dewatered by filter pads 60 before being discharged through valve 61 onto a conveyor 62 by which they are taken to storage.

COMPARATIVE TESTS OF PRESENT INVENTION AND U.S. PATENT No. 3,504,061.

These were carried out using the installation shown in Figure 1 with the tank 1 containing water 2 at approximately 48°F (9°C). Immersed within the tank was ramp 3 of aluminium 1/16 inch plate at an angle of 40°. Attached to the plate were three ultrasonic transducers 4 supplied by Dawes Instrument Co. Limited, which were operated at a power of [illegible] watts each at 25 Khz. Molten sulphur was poured at a temperature of 130/135°C in an unbroken stream 5 from a nozzle as shown in Figure 2 having an exit diameter 2 mm at a height of about 4 inches above the water surface. The stream of molten droplets contacted the ramp at about 6 inches below the water surface and was observed to have solidified after about 3 to 4 inches run along the ramp. The solidified pellets were removed from a sump 7.

In the following tests for mechanical stress pellets obtained by this process (SAMPLE A) were compared with pellets obtained by the swirled coolant process of U.S. Patent No. 3,504,061 (SAMPLE B).

Prior to the comparative tests the samples were allowed to age for 3 weeks. To assess the tendency of each sample to produce dust under mechanical stress, the samples were subjected to abrasion, compaction, impact and vibration tests. For the purposes of these tests particles passing through a 60 mesh screen (particle size below 250 microns) were considered to constitute dust. The values given in the Tables A and B for the % passing a given mesh size are Δ values, i.e. the % passing a given mesh after test minus the % passing that mesh in the sample before test.

Table A compares the 60 mesh Δ values (i.e. "dust") for each sample for each test. Table B shows the Δ values for a wider range of mesh sizes for each test.

The tests were performed as follows:

Abrasion.

To measure the effect of abrasion, the sulphur samples were tumbled in a V-mixer, thus minimizing impact of sulphur against the walls of the apparatus. A sample was placed in a "Plexiglas" (Registered Trade Mark) V-blender (Twin Shell Dry Blender Model LB—4264). The blender was operated at 9 rpm for a period of 2 hours. The sample was then retrieved and sieved.

Compaction.

The test for compaction involved submitting the sulphur samples to a pressure, based on the bulk density of formed sulphur, corresponding to a stockpile of approximately 100 ft. The sample in a suitable container was subjected in a hydraulic press for 10 minutes, to a pressure of 45 psi. Sieve analyses were carried out in the usual way.

Impact.

The effect of impact was measured by dropping samples onto an aluminium plate. Samples were dropped from a box having an appropriate trap door down a 12 inch diameter galvanized pipe and onto a 3/8 inch thick aluminium plate. A plastic bag was affixed around the base plate to ensure that no sample was lost. A drop height of 25 feet was used. Sieve analyses were carried out as described.

Vibration.

Solid sulphur is likely to be exposed to vibration in rail cars and ships' holds. The effect of this stress on the sulphur samples was tested by subjecting the samples to a vibration of 60 cps for one hour. Samples of the product under examination were placed in a four litre stainless steel beaker (inside diameter, 6 inches), covered, and taped to a "Syntron" (Registered Trade Mark) vibrating table, (Model VP 51—B). A hard rubber pad, ¼ inch thick, was placed under the beaker to prevent chatter, and the table was operated at 60 cps for one hour. A setting of 50% of maximum amplitude was used. Sieve analyses were carried out as described.

For each test 500 grams of material was used. Each test was performed in triplicate. The material prior to testing was screened through 18, 35, 60 and 100 mesh sieves corresponding to openings of 1,000, 5,000, 250 and 150 microns. The particle size distribution was recorded as cumulative percent passing each screen. Material passing the 100 mesh sieve was discarded. Following the test the sample was subjected to the same sieve analysis and the results were again tabulated as cumulative percent passing each screen.

Effect of Mechanical Stress Δ% Passing 60 Mesh

Sample	Abrasion	Compaction	Impact	Vibration	Total
A	0.1	0.1	1.3	0.1	1.6
B	0.1	0.2	2.5	0.2	3.0

TABLE B

Sieve Analysis After Individual Tests
Cumulative % Passing (Δ Values)

Sample	100	60	Mesh	35	18
	150	250	Microns	500	1000
			Abrasion		
A	0.1	0.1		0.1	0.8
B	0.1	0.1		0.1	0.2
			Compaction		
A	0.0	0.1		0.3	0.6
B	0.1	0.2		0.4	0.8
			Impact		
A	0.7	1.3		4.1	10.4
B	1.0	2.5		5.2	10.7
			Vibration		
A	0.0	0.1		0.1	0.3
B	0.1	0.2		0.3	0.4

Results.

As can be seen from the Tables, Sample A of the present invention showed improved results over Sample B (according to U.S. Patent No. 3,504,061). This is considered to be due to modification of the internal cavity inherent in the pellets produced by this latter process and general consolidation of the pellet under the influence of the ramp and ultrasonic pressure waves.

WHAT I CLAIM IS:—

1. A process for pelletizing sulphur comprising solidifying molten droplets in a coolant, wherein the solidifying pellets are brought into contact with an inclined ramp immersed in the coolant and/or the solidifying pellets are subjected to acoustic pressure waves.

2. A process according to Claim 1 wherein the acoustic pressure waves are generated by one or more ultrasonic transducer units.

3. A process according to Claim 1 wherein the acoustic pressure waves are generated by mechanical vibration.

4. A process according to any one of claims 1 to 3, wherein the acoustic pressure wave generator is coupled to the inclined ramp.

5. A process according to any one of claims 1 to 4, wherein the coolant is water.

6. A process according to any one of claims 1 to 5, wherein the molten sulphur is introduced into the coolant as droplets formed by a droplet-forming head.

7. A process according to any one of claims 1 to 5, wherein the molten sulphur is introduced into the coolant as a continuous stream and droplets are formed by the break-up of the stream within the coolant.

8. A process according to claim 7 wherein the unbroken stream is formed by the exit of molten sulphur from a reservoir through nozzles or gullies.

9. A process according to claim 8 wherein the nozzles have an exit bore diameter to exit bore length ratio of from 1.5 to 2.5:1.

10. A process according to Claim 1 substantially as described herein with reference to any one of Figs. 1 to 5 of the accompanying drawings.

11. Sulphur pellets obtained by a process according to any one of Claims 1 to 10.

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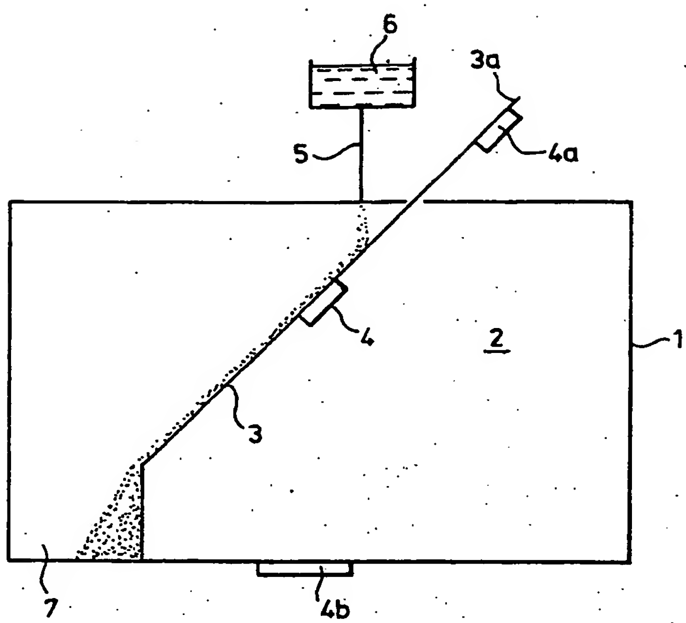

Fig.1.

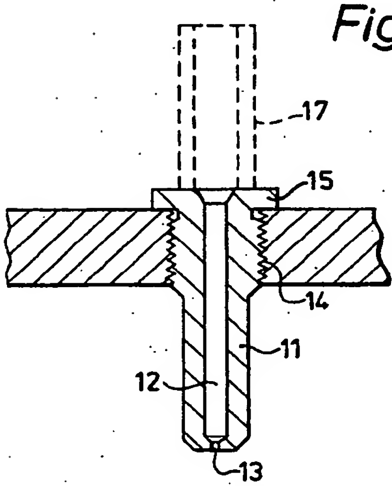

Fig.2a.

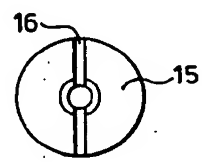

Fig.2b.

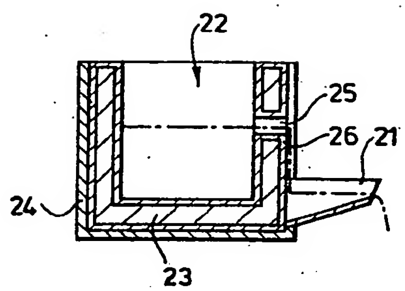

Fig. 3a.

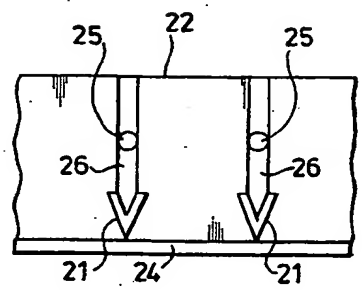

Fig. 3b.

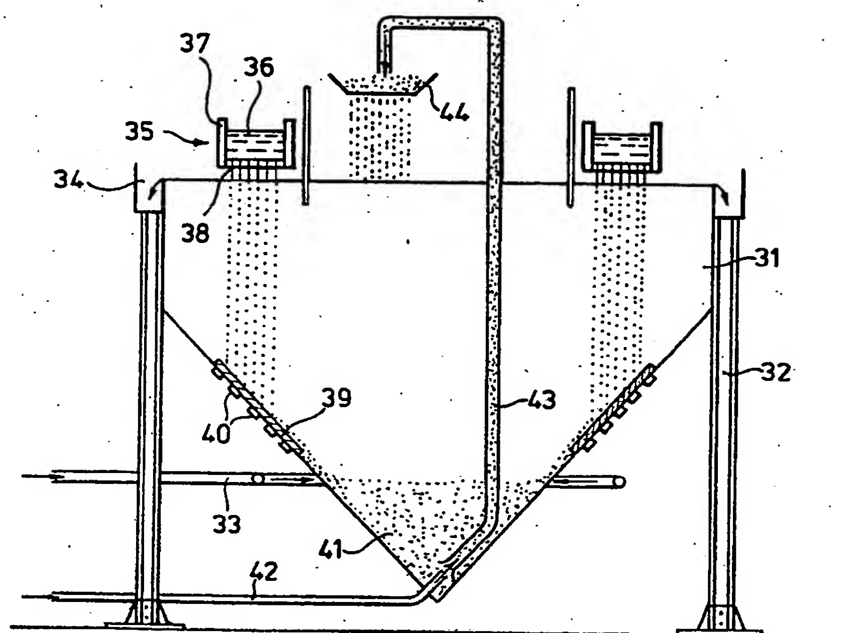

Fig. 4.

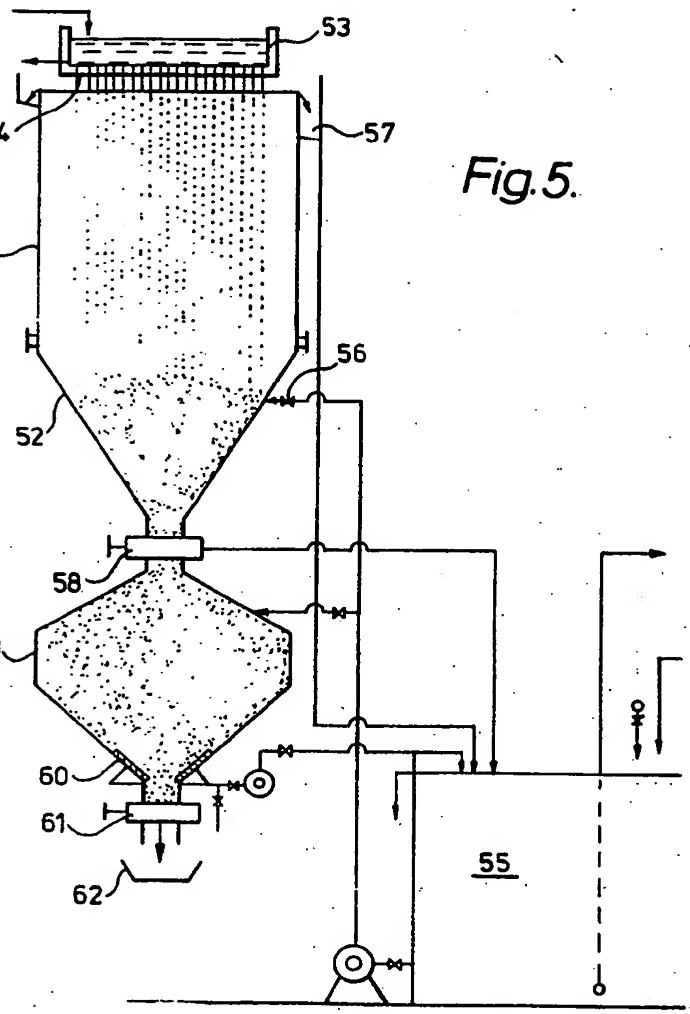

Fig.5.